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High PBDE Levels in Shorebird Eggs from the San Francisco Bay and Washington State

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Abstract

Concentrations of contaminants have been measured for decades and used as meaningful indicators of the relative health of populations of various species, and the ecosystems in which they live, across both space and time. The goal of this study was to assess aspects of the current health of nearshore coastal marine waters of the western United States by measuring various organic and heavy metal contaminant levels in appropriate trophic-level species. Seabirds are a particularly useful group of species to assess ecosystem health at various temporal and geographic scales because many species feed at high trophic levels, are long-lived, and typically are faithful to their breed sites. Therefore, in this study, we measured some heavy metal and organic contaminants in three upper trophic level obligate fish-eating seabirds (Forsters, Least and Caspian Terns) at various colonies along the west coast of the United States to: (1) assess differences in contaminant levels among different geographic breeding populations, and (2) compare these levels to historical contaminant data for these species. Specifically, we measured various polychlorinated biphenyls (PCBs), organochlorines, dioxins, a relatively new class of compounds of concern known as polybrominated biphenyl ethers, and three heavy metals (mercury, arsenic and lead). These data will be presented and discussed.

Introduction

High levels of polybrominated biphenyl ethers (PBDEs) have been found in humans and wildlife from the San Francisco Bay area ^{1,2}, with levels in women among the highest in the world, and levels in harbor seals doubling every 2-3 years². To further investigate the extent of contamination of the Bay area with PBDEs and their associated co-pollutants, 73 eggs of four species of fish-eating shorebirds were analyzed for levels of PBDEs, PCBs, PCDD/Fs, and PBDD/Fs. Shorebirds are useful for assessing ecosystem health at various times and places because they are at a high trophic level atop the marine food chain, are long-lived, and are faithful to their breeding sites. For comparison, measurements were made on eggs of shorebird species from the State of Washington.

Materials and Methods

53 individual eggs of four species and multiple nesting sites were provided by USFWS. Table 1 summarizes the species studied, the location of their nesting sites and the egg selection criteria.

Table 1. Species studied and the location of nesting sites

Common Name	Scientific Name	Nesting sites	Selection Criteria	Number of samples
Caspian Tern	<i>Sterna caspi</i>	Napa Marsh, Brooks Is., CA WA (4 sites)	Random	34
Forsters Tern	<i>Sterna forsteri</i>	Napa Marsh, Brooks Is., CA	Random	29
Least Tern	<i>Sterna antillarum</i>	Alameda NAS	Fail-to-hatch eggs	6
Clapper Rail	<i>Rallus longorostrus obsoletus</i>	North and South Bay sites	Fail-to-hatch eggs	4

The eggs were received frozen and were stored at -20° C until analyzed. The eggs were lyophilized, and moisture content was calculated by weight difference. The dried eggs were homogenized with a glass rod, and an aliquot representing 0.2 to 0.4 g of fat was spiked with nine ¹³C-PCBs; 15 ¹³C-PCDDs/Fs, and ¹³C- PBDE77 and then extracted by sonication and standing (3x) with 1:1 hexane: methylene chloride. A fraction of the extract was centrifuged, and "fat content" was determined by evaporating a known volume of supernatant extract to dryness. The remaining extract was passed over an mixed silica gel column and a carbon column (AX-21) in series. The eluate was labeled fraction 1, containing PCBs and PBDEs. The carbon column was eluted in the reverse direction with warm toluene, and this fraction, containing PCDD/Fs and coplanar PCBs, was labeled fraction 2. Both fractions were reduced to 5-7 ml and passed over an ABC Gel Permeation chromatographic column containing 60 g of BioBeads SX-2 with 357 ml of 1:1 hexane:methylene chloride, the final 170 ml of which was collected. This fraction was reduced to dryness with tetradecane keeper. After addition of recovery standard the samples were analyzed by HRGC/HRMS (Finnigan Mat 95). HRGC/MS was operated in EI multiple ion-monitoring mode with 9000 resolution. A 1 µL sample was injected onto a 60 meter, 0.25 µm film thickness DB 5 ms column in pulsed splitless mode.

Results and Discussion

ΣPBDE (of tetra to hepta-PBDEs) in the California egg samples averaged 6.2 ppm (fat based), with a range of 0.30 to 62 ppm. Five PBDE congeners (PBDE 47, PBDE 99, PBDE 100, PBDE 153, and PBDE 154), were found in all egg samples from SF Bay and Washington state. However, the hepta PBDE (PBDE 183) was not detected in any of the egg samples. In SF Bay samples, PBDE 47 was the predominant congener, averaging 4.1 ppm (66% of the total), followed by PBDE 99 (18%), PBDE 100 (11%), PBDE 153 (3%) and PBDE 154 (2 %). Analytical results are summarized in Table 2.

Table 2. PBDE levels (ng/g fat) in shorebird eggs from San Francisco Bay, CA (based on 53 California egg samples).

	Min	Max	Average	Median	STDEV	Ratio of PBDE#: ΣPBDE
Moisture%	74.0	79.1	77.1	77.4	1.19	
Fat%	30.7	41.5	38.25	38.43	2.21	
PBDE 47	129	52600	4116	2425	7260	0.66
PBDE 100	52.7	2920	658	452	630	0.11
PBDE 99	68.2	5650	1120	798	1110	0.18
PBDE 154	3.86	579	150	116	127	0.02
PBDE 153	1.67	895	163	115	172	0.03
Total PBDE	291	62400	6200	4410	8830	

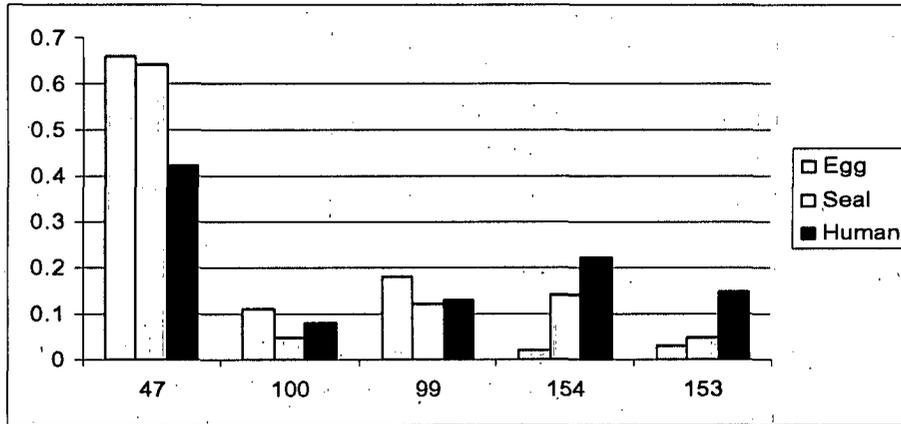


Figure 1. Relative congener patterns of PBDE in shorebird eggs, seals, and samples of human breast adipose, all from the San Francisco Bay Area.

Comparison of levels and profiles of PBDEs in humans, shorebird eggs, and seals from San Francisco Bay Area

The major congeners found in humans, shorebird eggs, and seals were the same: PBDE 47, 99, 100, 153 and 154. PBDE 47 was the dominant congener in all matrices. Σ PBDE concentrations were orders of magnitude higher in eggs (6 ppm) and seals (2 ppm) than in humans (86 ppb)^{1,2}.

PBDE 47 averaged about 65% of Σ PBDEs in both egg and seal samples, but only 42% in human adipose tissue samples, as can be seen in Figure 1. Hexa congeners (PBDE 153 and 154) appear proportionally lower in eggs and seals than in humans.

A subset of egg samples were tested for PBDDs, PBDFs and methoxy-PBDEs. No PBDDs, PBDFs and/or methoxy-PBDEs were found in the tested egg samples.

Comparison of levels and profiles of PBDEs in eggs from different species

Among eggs from the San Francisco Bay, 14 samples are from Caspian tern, 29 are from Fosters tern, 6 are from Least tern, and 4 are from Clapper Rail. The comparison of the levels and patterns of PBDE congeners from four species is shown in Fig. 2. Out of the four species, Fosters terns had the highest Σ PBDE, whereas the Clapper rail had the lowest Σ PBDE.

Comparison of levels and profiles of PBDEs in eggs from different locations

In addition to eggs from the San Francisco Bay, 20 eggs of Caspian terns from Washington State were also analyzed for PBDEs. Σ PBDEs in eggs from Washington State were lower than Σ PBDEs in eggs from San Francisco Bay. Table 3 compares the levels of PBDEs in eggs of Caspian terns from the San Francisco Bay and the State of Washington.

Table 3. Comparison of PBDE Levels in Caspian Tern Eggs from SF Bay and Washington State.

Washington State Eggs (n=20)						
	Min	Max	Average	Median	Std Dev	Ratio
Moisture %	75.8	79.1	77.5	77.5	0.79	
Fat %	30.7	41.5	38.5	39.0	2.31	
PBDE 47	1050	8840	2660	2070	1710	0.57
PBDE 100	266	1760	564	474	318	0.12
PBDE 99	542	3200	1210	1100	640	0.26
PBDE 154	44.2	349	96.8	80.4	65.3	0.02
PBDE 153	43.7	843	145	102	169	0.03
Total PBDE	1970	15000	4870	3920	2820	1.00

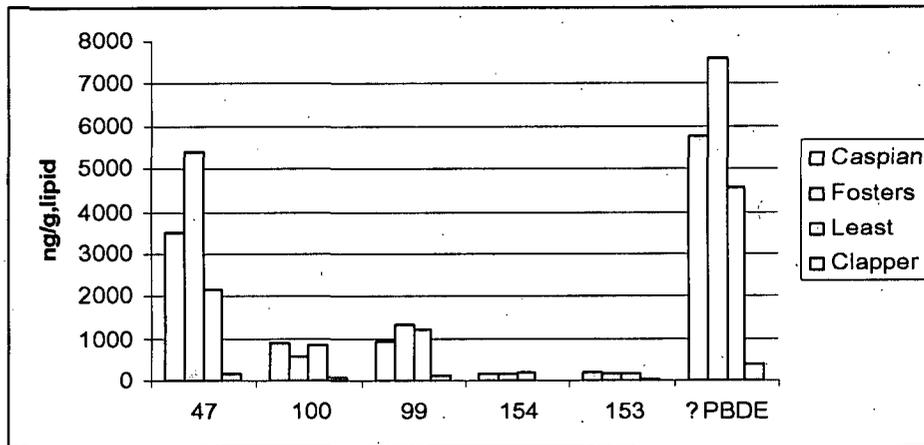


Figure 2. Comparison of levels of PBDEs in eggs from different species.

San Francisco Bay Area Eggs (n = 14)						
	Min	Max	Average	Median	Std Dev	Ratio
Moisture %	71.2	78.2	75.9	76.0	1.64	
Fat %	22.3	45.1	37.7	38.7	5.76	
PBDE 47	744	10500	3490	3100	2740	0.61
PBDE 100	185	2770	919	660	796	0.16
PBDE 99	238	2910	956	730	798	0.17
PBDE 154	39.2	499	168	124	137	0.03
PBDE 153	61.0	733	200	140	205	0.03
Total PBDE	1340	17300	5730	4680	4620	1.00

Comparison of levels of PBDEs and PCBs

Among the PCB congeners analyzed, levels of PCB 153 were the highest, averaging 4.4 ppm (fat based). As noted above, PBDE 47 averaged 4.1 ppm. These results suggest that the PBDE brominated flame retardants are fast becoming a newer version of the 'PCB problem'.

References

1. Jianwen She, Jennifer Winkler, Pat Visita, Michael McKinney, Myrto Petreas (2000), Analysis of PBDEs in Seal Blubber and Human Breast Adipose Tissue Samples, Organohalogen Compounds, 47, 53, 2000
2. Jianwen She, Myrto Petreas, Jennifer Winkler, Patria Visita, Michael McKinney, Dianne Kopec (2002), PBDES in the San Francisco Bay Area: measurements in the harbor seal blubber and human breast adipose tissue, 46, 697, 2002